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Field Gas Chromatography/Thermionic Detector System for On-Site Determination of Explosives in Soils

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Field Gas Chromatography/Thermionic Detector System for On-Site Determination of Explosives in Soils

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PREFACE

This report was prepared by Alan D. Hewitt and Thomas F. Jenkins, Research Chemists, Environmental Sciences Branch, U.S. Army Cold Regions Research and Engineering Laboratory (CRREL), Engineer Research and Development Center (ERDC), Hanover, New Hampshire; and by Thomas A. Ranney, Staff Scientist, Science and Technology Corporation, Hanover, New Hampshire.

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Field Gas Chromatography/Thermionic Detector System for On-Site Determination of Explosives in Soils

ALAN D. HEWITT, THOMAS F. JENKINS, AND THOMAS A. RANNEY

INTRODUCTION

Currently, there are two sets of on-site analytical methods—4050 and 4051, 8510 and 8515—recognized by the U.S. Environmental Protection Agency (U.S. EPA) for the determination of 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) in soil (U.S. EPA 1996–2000). These two analytes are the major ingredients in nearly all military munitions and subsequently are the most frequently detected nitroaromatic and nitroamine compounds in soil samples taken for characterization of explosives residues (Walsh et al. 1993). The analysis of soil samples with these on-site methods can serve to optimize off-site analysis (e.g., screen for sample blanks) with the knowledge that the concentration estimates for these two explosives are subject to interferences or the possibility of cross-reactivity, or both (Table 1 [Crockett et al. 1996]). For example, neither of the on-site methods for TNT can estimate the concentration of this analyte accurately when 1,3,5-trinitrobenzene (TNB), 2,4,6-trinitrophenylnitramine (tetryl), or the dinitrotoluenes (DNTs, 2,4- or 2,6-dinitrotoluene) are also present at similar concentrations. Therefore, before a definitive interpretation of on-site results can be made, an analyte-specific analytical method of analysis has to be performed. Another concern is that these on-site methods cannot determine the presence of the major biotransformation products of TNT, 4-amino-2,6-dinitrotoluene (4AmDNT) and 2-amino-4,6-dinitrotoluene (2AmDNT) (Jenkins et al. 1998). These are just a couple of the analyte selectivity issues that must be taken into account when determining whether these on-site methods can meet a project's data quality objectives. A more comprehensive discussion of the applications and limitations of these on-site techniques can be found elsewhere (Crockett et al. 1996, 1999).

Methods 8330 and 8095 are recommended by the U.S. EPA for the analysis of explosives samples sent to off-site laboratories (U.S. EPA 1994 and 1999). Both methods are capable of detecting a large suite of explosives analytes (Table 1). These more rigorous methods of instrumental analysis require analytical run times that exceed 15 minutes per analysis and use a soil sample preparation protocol that includes an 18-hour extraction in a cooled ultrasonic bath. Although these laboratory-based instrumental methods generally provide precise and accurate results, they inhibit site investigation activities because the time between sample collection and reporting of results often takes one or more weeks. In addition, there are several sample storage and transportation requirements that must be met.

The ability to quickly characterize the distribution of contamination in a large number of samples, and to reduce the number of very low concentration or nondetect samples sent off site for analysis, provided the incentives for developing on-site methods (Jenkins et al. 1996). These same criteria, along with the need to fill the gap between the capabilities of the existing on-site methods and those of the rigorous laboratory-based procedures, served as incentives for developing the on-site analytical method described here. To meet this analytical need we have been evaluating a field-portable gas chromatograph (GC) equipped with a thermionic ionization detector (TID [SRI, Torrance, California]) that is selective for compounds containing nitro (NO_2) functional groups (Hewitt et al. 2000). The instrument selection was based on the ability to determine the same suite of target analytes that can be determined using Method 8095 (GC-ECD [Walsh and Ranney 1998]), field ruggedness, and the need for minimal auxiliary support. Initially, both a nitrogen phosphorus detector (NPD) and electron capture detector (ECD) were also

Table 1. Methods for the detection of explosives recommended by the U.S. EPA.

<i>Method no./vendor</i>	<i>Analyte*: Interferences and cross-reactivities</i>
Method 8515 / EnSys RIS Method 8510 / EnSys RIS Method 4050 / D TECH	TNT: TNT = TNT + TNB + DNB + DNTs + tetryl RDX: RDX = RDX + HMX + PETN + NQ + NC + NG TNT: tetryl = 35%†; TNB = 23%; 2AmDNT = 11%; 2,4-DNT = 4%
Method 4051 / D TECH Methods 8330	RDX: HMX = 3% TNT, TNB, DNB, 2,4-DNT, 2,6-DNT, Tetryl, 2AmDNT 4AmDNT, NT (3 isomers), NB, RDX, HMX
Method 8095	TNT, TNB, DNB, 2,4-DNT, 2,6-DNT, Tetryl, 2AmDNT 4AmDNT, NT (3 isomers), NB, RDX, HMX, PETN, NG, 3,5-DNA

*Analyte abbreviations and names:

TNT—2,4,6-trinitrotoluene;
TNB—1,3,5-trinitrobenzene;
DNB—1,3-dinitrobenzene;
2,4-DNT—2,4-dinitrotoluene;
2,6-DNT—2,6-dinitrotoluene;
Tetryl—Methyl-2,4,6-trinitrophenylnitramine;
2AmDNT—2-amino-4,6-dinitrotoluene;
4AmDNT—4-amino-2,6-dinitrotoluene;
NT—ortho, meta, and para nitrotoluene;
3,5-DNA—3,5-dinitroaniline;
NB—Nitrobenzene;
RDX—Hexahydro-1,3,5-trinitro-1,3,5-triazine;
HMX—Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine;
PETN—Pentaerythritol tetranitrate;
NQ—Nitroguanidine;
NC—Nitrocellulose;
NG—Nitroglycerin.
†Percent cross-reactivity

evaluated for use with a field-portable GC. However, overall they were not found to be as sensitive or as selective as the TID detector (Hewitt and Jenkins 1999, Hewitt et al. 2000). The TID is an electrically heated emission source made in the shape of a bead composed of an alkali metal impregnated into a ceramic material (Patterson 1986). When compounds containing nitro functional groups impinge on the bead's surface, they are ionized, the negative ions move to a collector electrode, and the ion current at this electrode is measured with an electrometer. Therefore, this detector will respond not only to nitroaromatics and nitramines, but to nitrate esters as well. This report compares on-site GC-TID results to those obtained in the laboratory using either Method 8330 or 8095, for three different field trials.

METHOD AND MATERIALS

Instrumentation

In this study we used a field-transportable SRI Model 8610C gas chromatograph equipped with a heated (250°C) TID detector, a heated (225°C) on-column

injection port, and an internal air compressor. The instrument sells for less than \$9K, but also requires a personal computer (\$1K) for controlling the oven temperature program and for the collection and handling of data. Separations were performed on a Crossbond 100% dimethyl polysiloxane column, 15-m × 0.53-mm i.d., 1.5 µm (DB-1). Injections of 1 µL were made manually with a 10-µL glass syringe (SGE) equipped with an extra long needle (6.0 to 7.0 cm). The oven temperature program, carrier gas and flow rate, detector voltage, and the use of a supply of air to the detector were specific to the analytical objectives of the different field trials.

For the first field trial the target analytes were TNT, 2,4-DNT (2,4-DNT is a manufacturing impurity in the production of TNT), and two environmental transformation products of TNT, i.e., 2AmDNT and 4AmDNT. For this group of analytes a high level of sensitivity is achieved when using the settings originally recommended by the instrument manufacturer. Air was used as the carrier gas and the potential of the TID bead was set at -2.80 V (Hewitt et al. 2000). The air pressure for the on-board air compressor was set at 10 psi for a carrier gas flow rate of approximately 25 mL/min. The

oven temperature program for this application was 165°C for 1.5 min., ramp at 20°C/min. to 190°C, hold at 190°C for 1.25 min., allowing sample injections to be made about every 4.5 min. Figure 1 shows a typical chromatogram for 2,4-DNT, TNT, 4AmDNT, and 2AmDNT under these conditions.

At two other field trials the explosives analytes of concern included both nitroaromatics and nitramine explosives. The operating parameters for the analysis of both of these classes of explosives and nitrate esters were based on the results of laboratory studies and a preliminary field trial (Hewitt and Jenkins 1999, Hewitt

et al. 2000). For the simultaneous analysis of all three types of explosives, the sensitivity is improved by using ultra-high-purity nitrogen as the carrier gas and setting the TID potential at -3.40 V (Hewitt et al. 2000). The carrier gas pressure was set at 15 psi for an on-column flow rate of approximately 37 mL/min. Air was supplied to the detector from the onboard compressor at a flow rate of approximately 25 mL/min, with a pressure setting of 5 psi. An oven temperature program of 105°C, ramp at 10°C/min. to 115°C, ramp from 115°C to 240°C at 25°C/min., hold at 240°C for 0.75 min., allowed sample injections to be made about every 8.0 min. Figure 2 shows a typical chromatogram for these conditions.

Calibration standards

Analytical standards of 2,6-dinitrotoluene (2,6-DNT), 2,4-DNT, TNT, pentaerythritol tetranitrate (PETN), RDX, 4AmDNT, 2AmDNT, tetryl, and HMX were prepared from standard analytical reference materials (SARMs) obtained from the U.S. Army Environmental Center, Aberdeen Proving Ground, Maryland. The preparation and handling of mixed analyte working standards has been reported elsewhere (Hewitt and Jenkins 1999). In addition, all of the explosives analytes listed in Table 1 for Method 8330 were purchased as a mixed stock standard (each analyte 1.00 mg/mL), and nitroglycerin (NG) as a separate stock standard (5.00 mg/mL), from AccuStandard, Inc. (New Haven, CT). Both of these commercially prepared stock standards were specially prepared using acetone as the solvent.

Sample preparation

Sample collection, handling, and on-site preparation for analysis varied for each trial based on the data quality objectives. The soil samples ranged from 0.5 to 40 g and were extracted with an equal-to-a-fivefold-greater volume of acetone (i.e., 1:1 to 1:5). Extraction was performed in either glass or plastic bottles by manually shaking the soil-solvent slurry for 30 seconds or longer, then allowing the soil to settle. The total extraction period ranged from 5 to more than 30 minutes. The reduced ratio of sample weight to extraction solvent volume and short extraction period were used together when the main objective was to rapidly establish the presence of explosives residues. In general, field extraction periods of 30 minutes or longer are recommended for quantitative estimates of explosives residues in soils. Another general rule for quantitative explosives measurements is that, when extracting a moist soil, the volume of acetone should be at least twice the moist sample weight. Following extraction, an aliquot of the acetone was then drawn into a disposable plastic

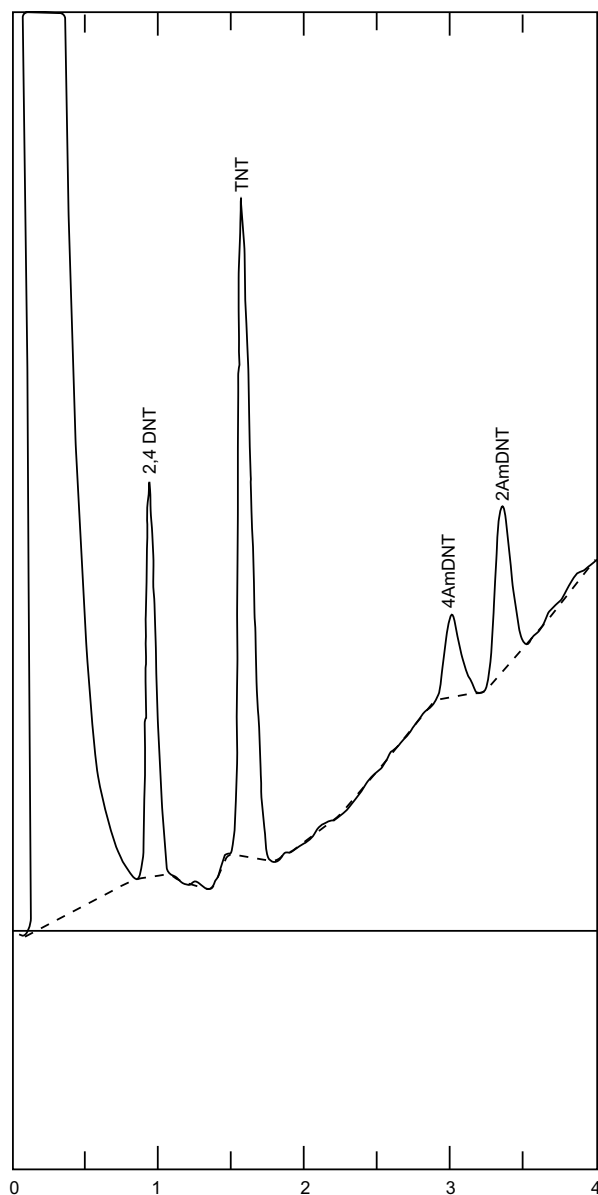


Figure 1. GC-TID chromatogram of 50 µg/L 2,4-DNT, TNT, and 2AmDNT, and 200 µg/L 4AmDNT.

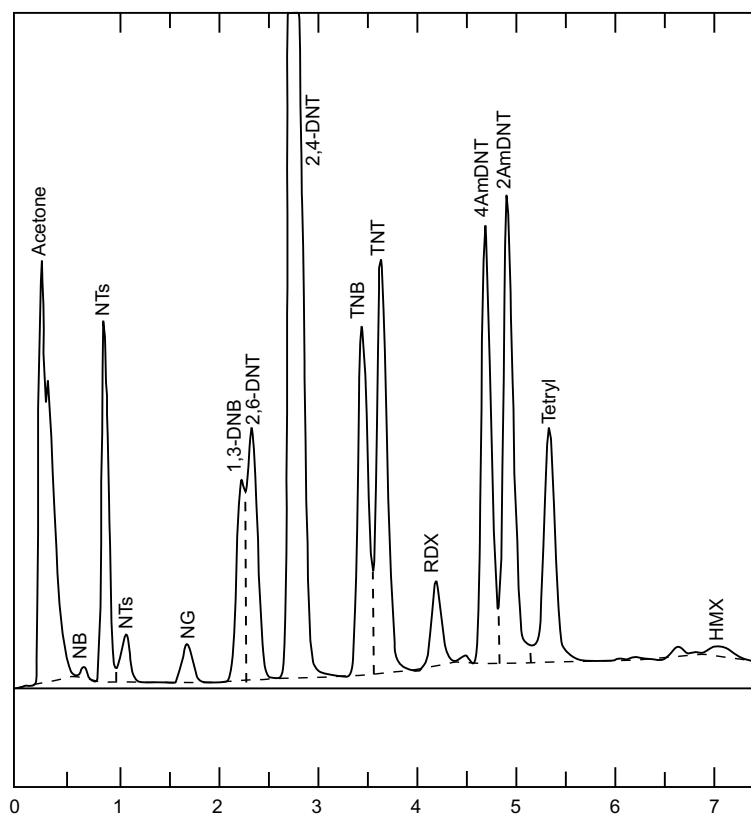


Figure 2. GC-TID chromatogram of 40 mg/L of the 8330 analytes and 200 mg/L of NG. Note: NTs—ortho, meta, and para nitrotoluene.

syringe and filtered by passing through a 25-mm Millex SR (0.5- μ m) filter that was attached via a Luer-Lok fitting. The filtered extract was directly transferred to a 2-mL amber deactivated glass vial.

Instrument calibration

With the exception of HMX, a five-point calibration curve was used for each trial and responses were based on peak heights. This number of standards allowed nonlinear models to be used when necessary. A nonlinear model (quadratic through the origin) was chosen when the linear regression through the origin failed to establish a correlation coefficient (r) of greater than 0.990. Continuing calibration checks were made after every five samples by randomly running one of the four highest standards. If the calibration model failed to establish a concentration within $\pm 20\%$ of the expected value for a standard, recalibration was performed. The concentration range used for calibration curves was selected based on the instrumental response to specific analytes, range of linearity, and the analytical objectives. Because of the poor sensitivity for HMX, a linear model calibration that was based on three of four points (Hewitt and Jenkins 1999) was used.

FIELD STUDIES

Fort Leonard Wood

The first field trial was performed at Fort Leonard Wood, Missouri, on April 17–19, 2000. At this site the objective was to rapidly establish the presence of explosives residues in soil samples collected near buried land mines. Previously it had been observed that 2,4-DNT, TNT, 4AmDNT, and 2AmDNT were detectable in soil samples collected above and near some of the land mines that contained TNT as the main explosive charge (Jenkins et al. 2000). When these analytes were detected in surface samples, the analyte concentrations were typically in the low (<100 μ g/kg) parts-per-billion range. During this field trial the GC-TID was set on a folding table inside of a building that was adjacent to the minefield. The calibration standards used ranged in concentration from 5 to 100 μ g/L for 2,4-DNT, TNT, and 2AmDNT, and from 20 to 400 μ g/L for 4AmDNT.

Duplicate, co-located soil samples were collected at every sampling location following the description given by Jenkins et al. (2000). One of the sample duplicates was analyzed on site and the other was returned to the Cold Regions Research and Engineering Laboratory

(CRREL) for Method 8330 and 8095 sample preparation and analysis. All of the samples were taken near buried mines after their exact location and orientation were established using a differential global positioning system, a template, and four metal tent stakes. The majority of samples was obtained by removing the first couple of millimeters of the ground's surface with a paint scraper after cutting away the vegetation with scissors. Because of the presence of vegetation (grass and weed roots, etc.) these samples often contained a large amount of organic matter. In some cases the mine was removed (unearthed). The soil samples that were obtained during a mine excavation were collected just above, below, and around the sides of the mine casing, and consisted mainly of mineral soil and small pebbles.

For on-site analysis, 0.5 to 3 g of soil/organic matter was transferred to a pre-weighed 20-mL glass scintillation vial, then returned to the on-site lab. After the vial was re-weighed to obtain the sample's moist weight an equal or two-times-greater volume of hardware-store-grade acetone was added using either a 0.500-mL syringe or 5-mL graduated cylinder. The low-sample-weight-to-extraction-solvent volume and short extraction period were used to optimize sensitivity and analysis speed. A greater than 1:1 ratio of acetone to sample weight, however, was needed when a large amount of organic matter was present. Once the acetone was added, the vial was capped, manually shaken at least twice for about 15 seconds, and then allowed to sit for 5 to 10 minutes. If organic matter was present, first a 3-mL Luer-Lok syringe (Becton Dickinson & Co.) with its guard cap in place was used to depress this debris below the solvent layer. Then, to collect at least 0.5 mL of the supernatant, the cap on the tip of the syringe was removed and the syringe was pressed into the organic matter slurry. When only soil was present in the sample vial a clear solvent layer often formed, from which a 0.5-mL or larger aliquot was withdrawn. The filtered sample extracts ranged in volume from 0.2 to 0.8 mL. Following on-site analysis, the sample extracts (about 70) were stored on ice and returned to CRREL, where a subset of the extracts was re-analyzed by GC-ECD (Method 8095) within two weeks of collection to evaluate the on-site results.

Umatilla Chemical Depot

The Umatilla Chemical Depot in Hermiston, Oregon, was visited on May 24–26, 2000. One of the characterization activities under way at this site was to identify where high concentrations (mg/kg) of TNT and RDX remained near the surface in an area that had been used for the open burning and open detonation (OB/OD) of obsolete munitions. These two explosives had been identified as principal contaminants of concern follow-

ing the preliminary investigations, which had used Method 8330 for sample preparation and analysis. However, other explosives residues were believed to be present as well. At this site the GC-TID was set up in the command post trailer on a folding table and nitrogen was used as the carrier gas. The calibration standard prepared for this site contained 2,6-DNT, 2,4-DNT, TNB, TNT, RDX, 4AmDNT, 2AmDNT, tetryl, and HMX. The calibration standards used ranged from 5.0 to 40 mg/L for HMX, 0.5 to 40 mg/L for 2,6-DNT and RDX, and 0.25 to 20 mg/L for the other six analytes.

The sampling plan for the OB/OD characterization activity called for a representative surface soil sample to be taken from each 20- × 20-ft subgrid in the region of concern. To accomplish this task the subgrid was divided into quadrants, and surface soil samples obtained from each quadrant were composited. After thorough mixing, a sample was taken by filling a 4-oz glass jar for subsequent on- or off-site (or both) analysis. All of the samples were stored in a refrigerator until processed on site for analysis by Methods 8515 and 8510. The first step for both of these on-site methods was to extract 20 g of soil with 100 mL of acetone in a plastic bottle. Following extraction an aliquot of the solvent was filtered. In addition to the filtered aliquot taken for Method 8510, a separate aliquot was transferred to a 2-mL amber deactivated glass vial and stored in a freezer for on-site GC-TID analysis. This additional aliquot of sample extract was obtained from about one quarter of the 437 samples scheduled to be processed. The analytical team from Dames and Moore, on contract to the Seattle District, Corps of Engineers, performed these sample preparation steps. In addition to these samples, soil and sediment samples that have been archived on site during other site characterization activities were made available for analysis, as were a couple of water sample extracts (solid phase extraction [Walsh and Ranney 1998]) from a groundwater treatment plant. After analysis, all of the sample extracts were stored in a freezer prior to shipment to CRREL. A subset of the sample extracts was re-analyzed by GC-ECD (Method 8095) at CRREL within two weeks of sample collection, to evaluate the on-site results.

Environmental Technology Verification Program (ETV)

The Environmental Technology Verification Program (ETV) was established by the U.S. Environmental Protection Agency to provide a third-party performance evaluation process for innovative or improved environmental technologies (www.epa.gov/etv). The ultimate objective of the ETV program is to expedite and facilitate the recognition of cost-effective technologies for use with environmental problems. This particular

evaluation was performed at the Oak Ridge National Laboratory (ORNL), in Oak Ridge, Tennessee, August 24–27, 2000, as part of the Site Characterization and Monitoring Technologies (SCMT) program, which is under the supervision of EPA's National Exposure Research Laboratory. This verification test evaluated the performance of technologies for on-site analysis of soils for explosives.

At the ETV test site the GC-TID instrumentation and a sample preparation station were set up on separate folding tables under a canopy with mesh netting on all four sides. During intermittent rainstorms a large tarp was pulled over the top of this canopy. For security reasons, each night the instrument and all supplies were returned to their shipping containers and stored inside a locked building. Auxiliary support consisted of an electrical extension cord run from a nearby building and a nitrogen gas cylinder. The description of the samples used for the ETV program stated that the primary explosives of concern would be TNT, 2,6-DNT, 2,4-DNT, RDX, and HMX at concentrations ranging from 0 to 90,000 mg/kg (ORNL 2000). The calibration standard used for this field study contained all of the Method 8330 analytes (Table 1) in concentrations ranging from 0.4 to 40 mg/L, dissolved in acetone, with the exception of HMX, which ranged from 2 to 40 mg/L.

The soil samples used for this ETV verification test were obtained from five different military facilities (ORNL 2000). Large bulk soil samples were shipped to ORNL for processing and characterization. These bulk soil samples were homogenized by kneading the material in the plastic shipping bags, transferring portions onto glass plates, subjectively removing debris, air-drying, passing through a 2-mm mesh sieve, then placing into a 1-L widemouth jar and thoroughly mixing with a metal spatula. Next the sample was removed from the bottle and quartered. Each quarter was further mixed, then a fourth of each quarter was recombined into new 1-L widemouth jars to yield four separate sample replicates, each of approximately 1000 g. Portions (20 to 40 g) were removed from each sample bottle and placed in a 4-oz glass sample jar for distribution to ETV participants and to a reference laboratory where Method 8330 sample preparation and analysis was performed. In addition, five matrix spike samples were purchased from a commercial reference standard vendor for distribution (ORNL 2000). These matrix spike samples were also distributed as quadruplicate subsamples. In total, 108 soil samples (27 quadruplicates) were extracted and analyzed. The samples were distributed on site in lots of 12 using a double-blind format, i.e., the sample jars were randomly numbered and the numbering was unique to each participant. The only information provided with the samples was the

site from which the soil had been originally obtained. However, this information was confounded by the random assignment of site locations to the blank and matrix spike samples.

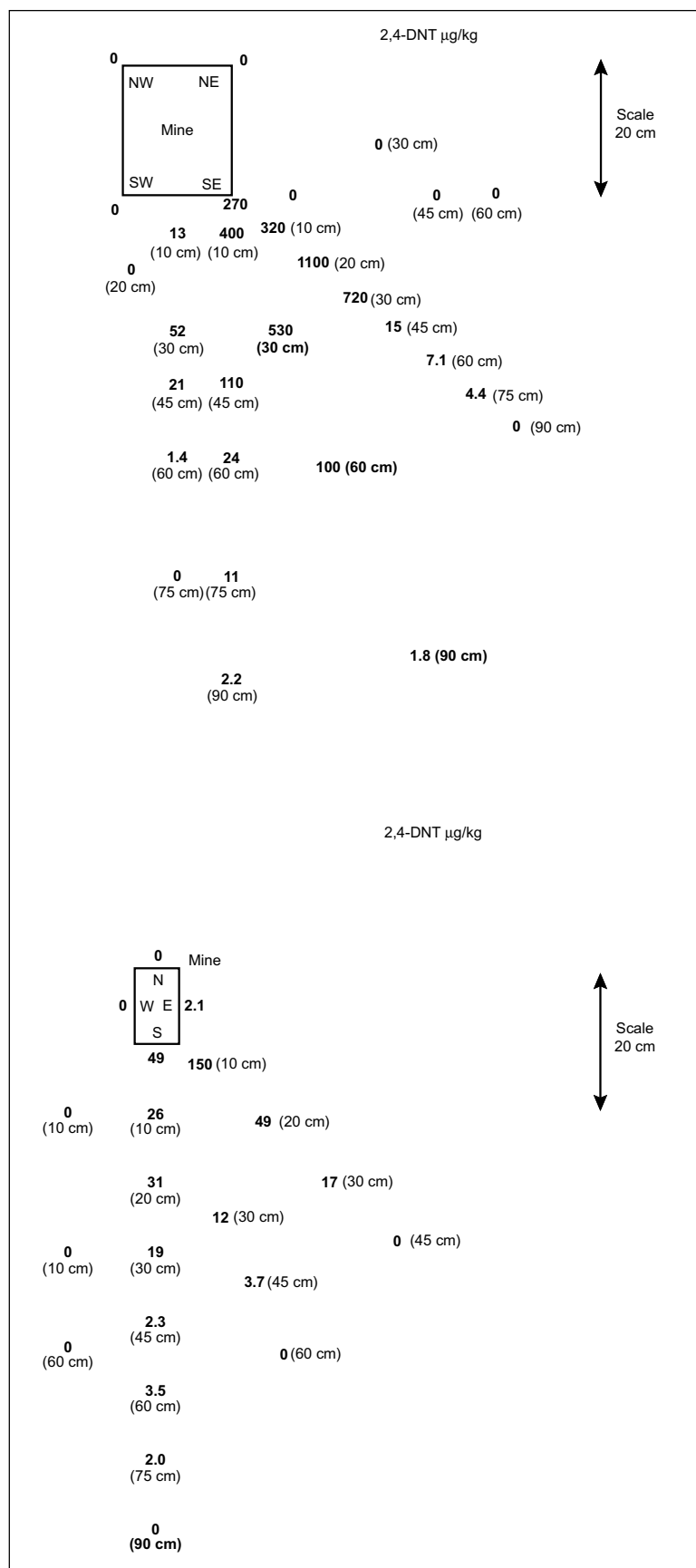
Samples were prepared on site by extracting 20 to 40 g of soil with a 40-mL volume of acetone. To measure the sample weight, the jar's contents were emptied into a disposable weighing dish, weighed, and then returned to the jar. Then 40 mL of acetone was added using an adjustable solvent dispenser. Extraction was performed by manually shaking the soil acetone slurry for several short intervals (2 min.) over a 30-minute period, then allowing the soil to settle. A 1.5-mL aliquot of the extract was filtered in preparation for analysis. To screen sample extracts for high concentrations of nitroaromatic compounds (e.g., TNT), a 0.25-mL volume was transferred to a clear 2-mL vial and 0.01 mL of a 5-mM tetrabutyl-ammonium hydroxide (TBAOH in water, the active reagent in Method 8515 [Aldrich]) solution was added. The formation of a dark purple or red solution provided a visual indication that a high concentration of nitroaromatic compounds was present. Depending on the color (i.e., the darker the color the greater the dilution) sample extracts were diluted anywhere from 1:10 to 1:2000, or not diluted at all, prior to analysis. All of the samples analyzed on site were refrigerated after analysis and returned to CRREL.

RESULTS AND DISCUSSION

Fort Leonard Wood

2,4-DNT, TNT, 4AmDNT, and 2AmDNT were detected in a number of surface and subsurface soil samples collected near buried land mines. Initially four surface samples were collected directly above the corners of buried land mines (Jenkins et al. 2000). For two of the mines, where mg/kg levels of explosives residues were detected in one or more of these initial samples, an extensive iterative sampling protocol was performed. Surface soil samples were sequentially collected while moving away from the established hot spot(s) in several directions, in increments of 10 cm. This sampling scheme and on-site analysis allowed us to delineate the size of the explosives-related chemical signature plume present at the ground's surface above these two buried land mines (Fig. 3). Before the development of this on-site analytical method, sample collection was performed using a set sampling design, which often was inefficient (the majority of samples collected had nondetectable explosives concentrations), and we were unable to delineate the boundaries of the surface plumes above these mines (Jenkins et al. 2000). However, this earlier work had established that the ex-

Figure 3. Surface concentration ($\mu\text{g/kg}$) of 2,4-DNT near two buried land mines.



plosives signatures at the surface were spatially heterogeneous.

Of the sample extracts analyzed on site and also returned to CRREL for analysis by GC-ECD (Method 8095), only those that had an extract volume of 0.3 mL or greater could be reanalyzed. This sample volume limitation was necessary because of the capabilities of the HP auto sampler used with the HP 6890 GC-ECD. Table 2 shows the concentrations ($\mu\text{g/kg}$) obtained for 2,4-DNT, TNT, 4AmDNT, and 2AmDNT by both GC-TID and GC-ECD analysis for those sample extracts that were analyzed both on site and in our laboratory. Also included in this table are the median and range of the percent differences (%D) of the field results as compared to the laboratory results. This comparison shows that the median percent differences for 2,4-DNT, 2AmDNT, and 4AmDNT were less than 10%. The TNT values established in the field with GC-TID, however, were biased high. One explanation for this discrepancy is that TNT at these low concentrations (less than 250 $\mu\text{g/kg}$) was not stable in the acetone extracts, therefore the TNT concentrations may have decreased between

the two analysis times.* To test this hypothesis, 10 archived soils were extracted using the protocol used at Fort Leonard Wood, then sequentially analyzed on the same day by both GC-TID and GC-ECD. Table 3 shows the concentrations ($\mu\text{g/kg}$) of 2,4-DNT and TNT obtained by these two methods of analysis. The good agreement (low median %D) for both analytes is consistent with the hypothesis that the discrepancy in the TNT values for the Fort Leonard Wood samples was due to TNT degradation during the time between on-site and laboratory analysis (seven to 10 days).

Umatilla Chemical Depot

Most of the samples analyzed on site at the Umatilla Chemical Depot were obtained during the characterization of an area that had been used for the OB/OD of munitions. Furthermore, prior to the analysis by GC-TID, several of the samples had been identified as hav-

*Personal communication, Marianne E. Walsh, Chemical Engineer, CRREL, Hanover, New Hampshire, May 2000.

Table 2. Comparison between GC-TID-1 field and GC-ECD laboratory (Method 8095) results for explosives in solvent extracts of samples collected at the Fort Leonard Wood minefield.

Analyte concentration ($\mu\text{g/kg}$)								
2,4-DNT		TNT		4AmDNT		2AmDNT		
TID-1	ECD	TID-1	ECD	TID-1	ECD	TID-1	ECD	
1.	270	240	18	9.5	350	240	320	250
2.	320	370	25	18	320	370	470	490
3.	1100	1300	220	180	2200	2500	2800	3000
4.	7.1	7.9	ND	0.8	ND*	19	44	42
5.	4.4	3.7	ND	ND	22	9.9	21	17
6.	ND	ND	ND	ND	ND	2.9	ND	3.2
7.	49	47	26	3.8	190	170	180	160
8.	26	27	12	2.5	100	100	110	96
9.	31	28	13	1.6	42	65	96	68
10.	17	21	5.4	1.2	41	31	35	38
11.	3.5	3.8	1.5	0.8	ND	8.4	7.2	10
12.	ND	0.7	ND	ND	ND	2.4	ND	3.5
13.	360	410	120	15	IF†	310	310	380
14.	110	94	9.5	1.5	170	150	350	260

Median and range of the % differences for analysis pairs (ECD reference value) with analyte concentrations.

2,4-DNT		TNT		4AmDNT		2AmDNT	
Median	-5.79		365		5.88		8.63
Range	-19.0 to 18.9		22.2 to 712		-35.4 to 122		-28.0 to 41.2

*ND—Not detected

†IF—Peak interference

Table 3. Comparison between GC-TID and GC-ECD laboratory (Method 8095) results for explosives in solvent extracts of archived soil samples collected at military facilities. Sample extracts were analyzed by both methods at the same time.

	Analyte concentration ($\mu\text{g/kg}$)			
	2,4-DNT		TNT	
	TID	ECD	TID	ECD
1.	140	130	47	47
2.	4.3	7.6	51	77
3.	290	300	290	320
4.	ND	ND	ND	1.1
5.	ND	0.8	0.8	1.7
6.	18	19	92	110
7.	7.5	8.8	0.7	0.7
8.	420	420	2.1	1.2
9.	9200	8000	28	32
10.	9.3	9.5	250	220

Median and range of the % differences for analysis pairs (ECD reference value) with analyte concentrations.

	2,4-DNT	TNT
Median	-2.72	-4.0
Range	-43.4 to 15.0	-33.8 to 75.0

ing high levels of TNT or RDX, or both, by Methods 8510 and 8515. Several explosives analytes were detected in these soil samples, as well as the archived sediment samples and water sample extracts that were made available for analysis. The most frequently detected analytes by GC-TID were 2,4-DNT, TNB, TNT, RDX, and HMX. Table 4 shows the values obtained by both GC-TID performed on site and GC-ECD (Method 8095) subsequently obtained in our laboratory at CRREL for TNB, TNT, and RDX.

The results in Table 4 show good agreement (median percent difference values of less than 13%) between the two methods of analysis for TNB, TNT, and RDX. The reduction of TNT in the acetone extracts did not appear to occur as it had for the samples returned from Fort Leonard Wood. Perhaps TNT is more stable in acetone at the higher concentrations typical of these samples, or perhaps the storage condition (storage in a freezer versus on ice) used for these samples was better. 2,4-DNT was not included in this table because it was present only at concentrations below the lowest calibration standard used during this field demonstration. A couple of problems were encountered with the GC-TID estimates for HMX, i.e., false positives (three out

of 10 cases) or values considerably higher ($3\times$, 3 out of 10) than the Method 8095 results. The GC-TID chromatograms that resulted in false positives or biased high HMX concentrations often had a very broad peak for this explosive. This poor peak shape most likely is an indication that background interferences were present.

One of the more interesting findings of this field trial was that, while the GC-TID results agreed with the Method 8515 results for TNT, more often than not they did not agree with the Method 8510 results for RDX. In those samples where Method 8510 obtained a response for RDX that resulted in a concentration that was not confirmed by GC-TID analysis, the GC-TID chromatograms showed a peak(s) that eluted before 2,6-DNT or just before RDX, or both. Analysis of these same sample extracts in the laboratory by both GC-ECD and GC-TID established that the peak appearing before 2,6-DNT was NG while the peak on the front edge of the RDX peak was PETN. Both NG and PETN are analytes that give a positive response when using Method 8510 (Crockett et al. 1996). Therefore, by using the GC-TID, these analytes and HMX, all of which give a positive response by Method 8510, could be resolved.

Table 4. Comparison between GC-TID field and GC-ECD laboratory (Method 8095) results for explosives in solvent extracts of soil and sediment samples collected at the Umatilla Chemical Depot.

	<i>Analyte concentration (mg/kg)</i>					
	<i>TNB</i>		<i>TNT</i>		<i>RDX</i>	
	<i>TID</i>	<i>ECD</i>	<i>TID</i>	<i>ECD</i>	<i>TID</i>	<i>ECD</i>
1.	ND	ND	480	430	ND	ND
2.	ND	ND	2900	3700	ND	ND
3.	ND	ND	0.25	0.11	ND	1.1
4.	ND	ND	5.8	4.6	ND	0.4
5.	ND	ND	980	780	ND	ND
6.	ND	ND	520	440	ND	ND
7.	ND	ND	0.20	0.30	ND	ND
8.	ND	ND	15	14	ND	ND
9.	2.2	3.2	18	19	ND	ND
10.	18	16	220	210	ND	ND
11.	ND	ND	1000	840	ND	ND
12.	ND	ND	ND	ND	31	25
13.	22	14	40	33	ND	ND
14.	ND	ND	620	550	400	380
15.	0.2	ND	0.25	0.40	12	9.4
16.	ND	ND	1100	870	ND	ND
17.	3.2	4.3	0.10	0.16	6.0	5.4
18.	4.2	5.1	0.20	0.23	5.6	5.1
19.	50	36	1100	920	440	320
20.	49	26	1100	1000	440	430
21.	ND	ND	15,000	14,000	5900	6000
22.	ND	ND	20,000	16,000	8000	6700

Median and range of the % differences for analysis pairs (ECD reference value) with analyte concentrations.

	<i>TNB</i>	<i>TNT</i>	<i>RDX</i>
Median	12.5	11.6	11.1
Range	-31.2 to 88.5	-37.5 to 127	-1.67 to 37.5

Environmental Technology Verification Program (ETV)

The on-site GC-TID and off-site reference laboratory results for 2,4-DNT, TNT, and RDX are given in Appendix A. A cursory review of the values reported in Appendix A turned up two aberrant values reported by the off-site reference laboratory (Blank 2-Replicate 2 and Iowa 1-Replicate 2). These values were most likely due to operator error (ORNL 2000). Both the reference laboratory and the on-site GC-TID analyses were 100% complete, since values were reported for every sample. In the following discussion, we compare the analytical results from the on-site GC-TID analyses with those from the reference laboratory using Method 8330. Once publicly available, an independent evaluation of the GC-TID performance in the form of a verification report can be found on the ETV web site.

The ETV samples included 20 soil samples spiked with TNT and RDX to assess accuracy (% recovery). A summary of results for both the GC-TID and a reference laboratory analysis is presented in Table 5. Based on the mean values, both the reference laboratory and GC-TID were unbiased. However, when comparing the individual values to the acceptance criteria established by the developer (Environmental Resource Associates, Arvada, Colorado), the reference laboratory reported more outliers than the GC-TID (Table 6). For example, the reference laboratory reported two values for both RDX and TNT that were higher than the expected concentration by 35% or more (Appendix A, Spike/PE, Sample 5-Replicate 2 and Sample 6-Replicate 3). All four of these reference laboratory values and two other high values failed to meet the acceptance criteria that were set for these standard reference materials. In con-

Table 5. ETV program GC-TID and reference laboratory accuracy (% recovery) based on spiked soil samples (n = 20).

Statistic	GC-TID		Reference laboratory*	
	TNT	RDX	TNT	RDX
Mean	97	91	100	102
Median	96	90	96	99
Range	87–110	74–112	76–174	84–141

*Reference laboratory used Method 8330.

trast, only two GC-TID values were outside of the acceptance criteria range (Table 6). Therefore, the reference laboratory showed a tendency to report individual values that were biased high even though their mean recovery was approximately 100%. To assess precision, the relative standard deviations were tabulated for all of the sample quadruplicates (environmental and reference samples) that had values reported above the detection limit (0.5 mg/kg or above) for each of the repli-

cates (Table 7). This evaluation shows that the GC-TID tended to be more precise. However, the ranges of the %RSDs were comparable.

Twenty blank soil samples were analyzed during the ETV verification test. Five false positives (25%) were obtained by the GC-TID for TNT, while the reference laboratory reported only two (10%) false positives for TNT (Table 8). Not taking into consideration the apparently aberrant value (Appendix A, Blank 2-Repli-

Table 6. Number of GC-TID and reference laboratory spiked soil results within acceptance range set by Environmental Resources Associates (ERA, Arvada, CO.).

A. TNT			
Number of results within range*			
Spike (mg/kg)	Accpt. range	GC-TID TNT	Reference laboratory† TNT
10	7–13	4	4
50	35–63	4	4
100	70–126	4	4
250	174–315	4	3
500	348–630	4	3
B. RDX			
Number of results within range			
Spike (mg/kg)	Accpt. range	GC-TID RDX	Reference laboratory RDX
10	8–11	3	4
50	38–57	4	3
100	76–113	3	3
250	190–282	4	3
500	379–566	4	3

*Total number of samples spiked at each concentration n = 4.

†Reference Laboratory used Method 8330.

Table 7. ETV program GC-TID and reference laboratory precision (% RSD) for soil sample replicates (quadruplicates).

Statistic	GC-TID			Reference laboratory*		
	2,4-DNT	TNT	RDX	2,4-DNT	TNT	RDX
	<i>n</i> = 4†	<i>n</i> = 17	<i>n</i> = 13	<i>n</i> = 3	<i>n</i> = 18	<i>n</i> = 13
Mean	15	23	14	56	29	25
Median	9.0	13	10	32	25	21
Range	9–31	2–107	5–44	12–123	2–72	4–63

*Reference laboratory used Method 8330.

†Mean is based only on sample sets where all four replicates had values reported.

cate 2), only one of the remaining false-positive values for both methods of analysis was greater than 1.1 mg/kg. The carryover of TNT and other explosives, because of cold spots in the injection port of the GC-TID system, continues to be a concern even after adding a heated injection port to the GC (Hewitt and Jenkins 1999). High concentrations of TNT could not be avoided completely during the ETV verification test because of the necessity to analyze for RDX in the same sample extract. Therefore, even with the addition of a heated injection port and screening samples prior to analysis, carryover appears to remain an issue of concern. This problem is not unique to this GC system, and perhaps with further design changes it will become less of an issue in the future.

The experimental design also allows for comparability testing between the GC-TID and laboratory results for each individual sample that had analyte concentrations estimated above 0.5 mg/kg by both methods. For this comparison there were 12, 52, and 69 comparable data points for 2,4-DNT, RDX, and TNT, respectively (aberrant TNT laboratory value removed). The correlation coefficients and slopes for the comparison of these data points for 2,4-DNT, RDX, and TNT were, respectively, $r = 0.44$ and $m = 0.33$, $r = 0.85$ and $m = 0.91$, $r = 0.95$ and $m = 1.32$. An additional analysis

of RDX and TNT value comparability between the two analyses was performed by assessing the ranges of %D. However, it should be recognized that in addition to variability due to sample preparation and analysis, there is variability (heterogeneity) in the analyte distribution within the sample jar from which the subsamples were removed for analysis by each participant and the reference laboratory. With respect to the homogeneity of these analytes in each sample jar, RSDs of 20% or less were estimated for five replicate measurements (ORNL 2000). This information does not readily lend itself to setting an appropriate range for the %D, for judging acceptability. With ± 25 %D as the acceptance criterion, 65% of the RDX and 45% of the TNT results are within range, whereas 96% of the RDX and 83% of the TNT results are acceptable for ± 50 %D. Both of these comparisons (regression analysis and %D) show that, in general, there was good agreement between the two methods of sample preparation and analysis for both RDX and TNT (Fig. 4 and 5), and poor agreement for 2,4-DNT.

In an attempt to understand the discrepancy between the GC-TID and reference laboratory results for 2,4-DNT, the set of the samples that had been determined to have this explosives analyte were reanalyzed by Method 8330 at CRREL (Table 9). This analysis was

Table 8. ETV program GC-TID and reference laboratory false-positive results for blank soil samples (*n* = 20).

Statistic	GC-TID			Reference laboratory*		
	2,4-DNT	TNT	RDX	2,4-DNT	TNT	RDX
No. FP†	0	5	0	0	2	0
% FP	0	25	0	0	10	0

*Reference laboratory used Method 8330.

†False-positive value reported.

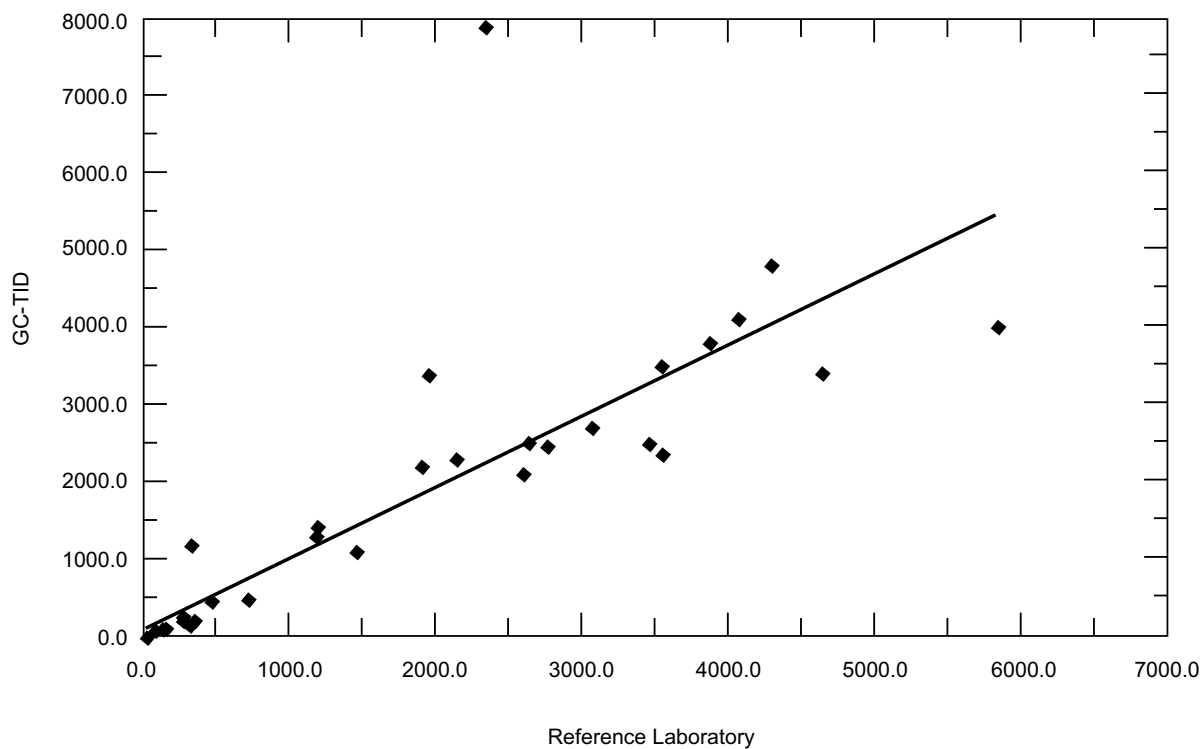


Figure 4. Comparison of RDX values (mg/kg) established on site with GC-TID analysis and by Method 8330 at a reference laboratory ($r = 0.85$, $m = 0.91$).

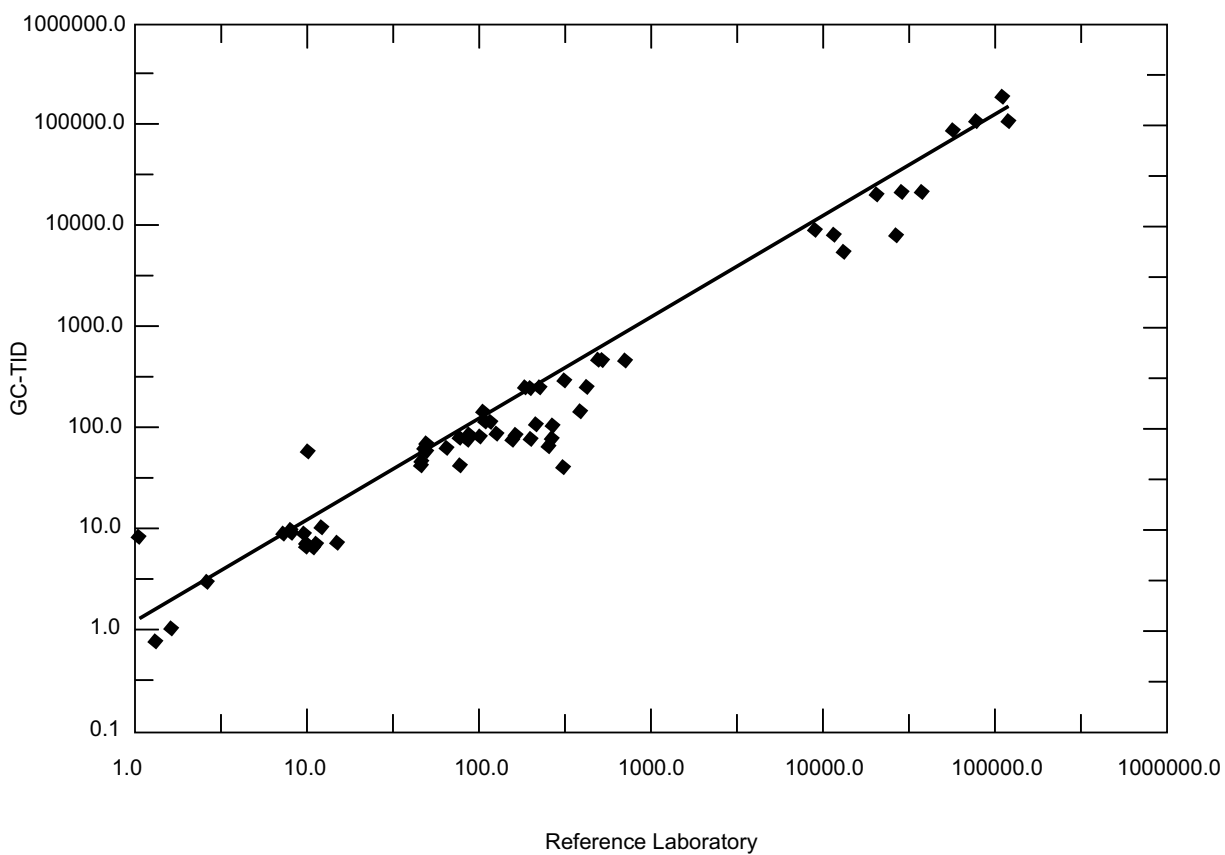


Figure 5. Comparison of TNT values (mg/kg) established on site with GC-TID analysis and by Method 8330 at a reference laboratory ($r = 0.95$, $m = 1.32$).

Table 9. Comparison between on-site GC-TID and CRREL laboratory (Method 8330) results for TNT and 2,4-DNT in solvent extracts of ETV soil samples.

	Analyte concentration (mg/kg)			
	2,4-DNT		TNT	
	TID	HPLC	TID	HPLC
1.	14	16	80	85
2.	8.8	9.4	84	81
3.	8.5	10	82	82
4.	7.2	9.8	73	84
5.	0.7	0.69	7.7	6.5
6.	0.6	0.65	7.3	6.4
7.	0.7	0.80	7.1	7.0
8.	0.6	0.73	6.8	6.7
9.	0.7	0.72	9.9	8.6
10.	0.7	0.72	8.0	6.9
11.	0.6	0.62	7.7	6.4
12.	0.6	0.74	7.7	7.7

Median and range of the % differences for analysis pairs (HPLC reference value).

	2,4-DNT	TNT
Median	-10.1	2.6
Range	-26.5 to 1.45	-13.1 to 20.3

performed on the same sample extracts that had been prepared and analyzed on site by GC-TID. Table 9 also includes the TNT values obtained, to indicate that analyte concentrations had remained stable during storage. A review of the results in this table shows that CRREL-HPLC results were consistent with the on-site GC-TID results for both TNT and 2,4-DNT. The poor agreement found for 2,4-DNT between the on-site GC-TID and reference laboratory perhaps was an artifact of the low number ($n = 12$) of data points and small range of concentration (0.5 to 50 mg/kg). Close inspection of the results for 2,4-DNT shows two apparent trends: 1) as was true for the other two explosives, the GC-TID values for the sample quadruplicates were more precise than the reference laboratory (one of the reference laboratory quadruplicate sets had the highest %RSD [122%] for this comparison study); 2) the reference laboratory concentration estimates were higher than for the GC-TID. However, the only way to resolve which set(s) of analyses is more likely to be correct would have been to include some soil samples spiked with 2,4-DNT so that an assessment of accuracy could be performed.

Values for tetryl in these soil samples were obtained during the ETV verification test, and the same sample

extracts were reanalyzed back at CRREL by both GC-TID and GC-ECD (Table 10). The GC-TID analysis was performed a second time, just prior to GC-ECD analysis, because this analyte is known to be unstable.* Even though this is a limited data set ($n = 8$), a median %D value of less than 26% indicates that there was reasonable agreement between the two methods of analysis for tetryl. The reference laboratory failed to report tetryl values above 0.5 mg/kg for these same samples.

Prior to participation in the ETV verification test, six pre-demonstration samples were distributed for analysis. These soils, which had been extensively analyzed by ORNL using Method 8330, were analyzed at CRREL by GC-TID. Table 11 shows the HMX results obtained for five of these samples (the sixth sample contained no HMX). The GC-TID results for HMX in this table were very promising. However, during the ETV program, values for HMX were not reported because of the inability to consistently establish a response for this analyte that systematically increased over the chosen calibration range. Failure to consistently achieve

*Personal communication, Marianne E. Walsh, Chemical Engineer, CRREL, Hanover, New Hampshire, October 2000.

Table 10. Comparison between GC-TID (field and laboratory) and GC-ECD laboratory (Method 8095) results for tetryl in solvent extracts of ETV soil samples.

	Tetryl (mg/kg)		
	GC/TID		ECD
	On site	Lab	Lab
1.	15	12	11
2.	0.6	1.1	0.9
3.	18	16	13
4.	3.0	3.4	3.8
5.	87	73	52
6.	44	40	38
7.	35	33	27
8.	23	24	19

Median and range of the % differences for analysis pairs (ECD reference value, and the on-site GC-TID) with analyte concentrations.

	Tetryl
Median	25.3
Range	-33.3 to 67.3

a change in response between the 40 and 20 mg/L calibration standards was an anomaly unique to the ETV verification test. Foremost, it should be noted that because HMX has a very low vapor pressure, it is one of the most difficult explosives analytes on the 8330 analyte list to determine by GC (Walsh and Ranney 1998, Hewitt et al. 2000). Indeed, this compound tends to degrade in the injection port and as it passes through the chromatographic system. A possible factor in the poor performance of the GC-TID to analyze HMX on-

site was the environmental conditions under which this instrument was operated during the ETV verification test. The instrumentation was often exposed to direct sunlight and the average temperature and humidity were 83°F and 58%, respectively. These environmental conditions may further challenge this instrument's ability to detect HMX. Recently, it was observed that an oven program of 145°C, hold for 0.75 min., ramp to 170°C at 20°C/min., ramp to 230°C at 30°C/min., ramp to 245°C at 10°/min., improved the response for HMX (sharper peak [Fig. 6]). Using this temperature program, several of the sample extracts were reanalyzed by GC-TID at CRREL. Samples were selected after receiving the HMX values estimated by the reference laboratory. Table 12 shows that comparison of the HMX concentration estimates for both laboratories is again very promising, as it was for the pre-demonstration samples.

SUMMARY

During three separate field trials the GC-TID was observed to be a robust field analytical system capable of producing results comparable to Methods 8330 and 8095 for the determination of several explosives compounds in soil. In particular, participation in EPA's Environmental Technology Verification Program, a well-orchestrated and designed third-party evaluation, demonstrated that this on-site method produced results that were in very good agreement with those from a reference laboratory using Method 8330. Indeed, a close inspection of the data shows that the on-site GC-TID method provided more accurate results for reference samples and showed better overall precision for the environmental and reference samples than the reference laboratory using Method 8330.

Table 11. Pre-demonstration results for HMX. Samples labeled C-1 and C-2 are duplicates, as are D-1 and D-2.

	Soil results for HMX (mg/kg)				
	Blank	C-1	C-2	D-1	D-2
Anticipated result	0	297	297	458	458
Acceptance range	0	151-443	151-443	240-676	240-676
*ORNL	<1.0	316	301	381	408
GC-TID	<2.5	220	380	460	400

*ORNL used Method 8330.

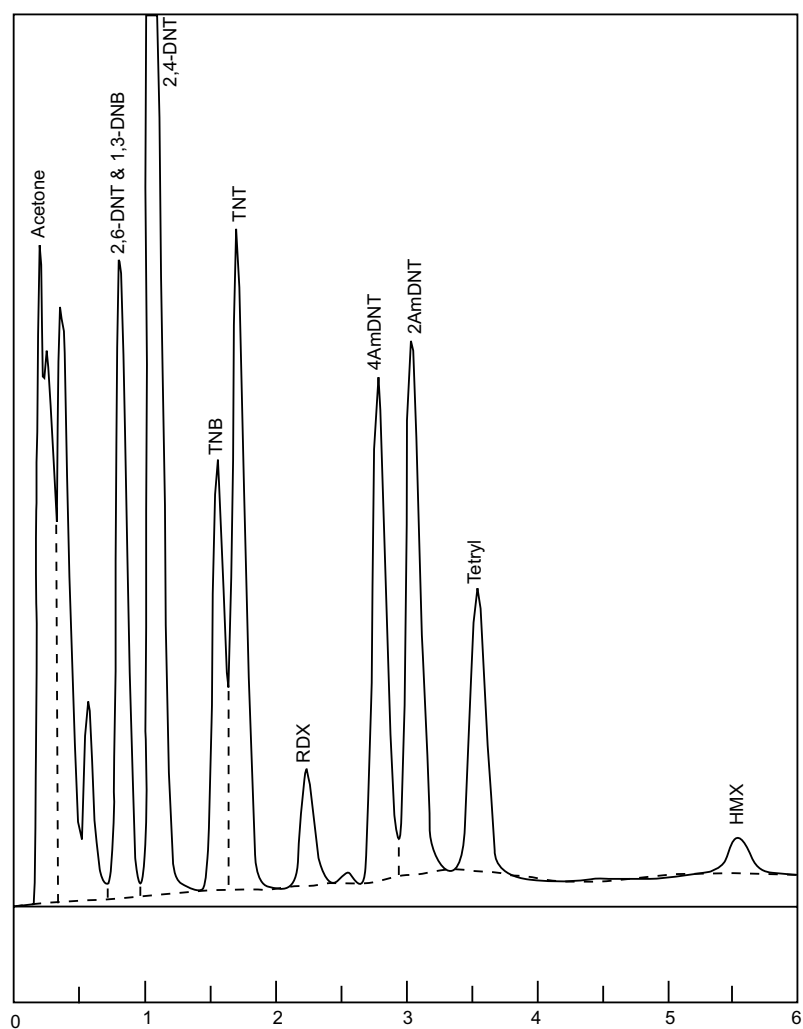


Figure 6. GC-TID chromatogram of 40 mg/L of the 8330 analytes.

Table 12. Comparison between GC-TID laboratory and reference laboratory results for HMX in selected ETV samples.

Sample	(HMX mg/kg)	
	TID	Ref lab*
1050	240	370
1073	200	252
1092	230	259
1013	200	264
1034	200	278
1031	180	248
1098	240	322
1067	230	185
1026	280	300
1084	210	185
1066	300	392
1030	240	214
1097	12	22.2
1019	16	23.2
1083	15	16.5
1039	22	42
1014	1.7	8.3
1074	3.0	3.6
1064	2.8	3.5
1072	2.5	4.3

*Method 8330

Use of the on-site GC-TID method is compatible with the use of dynamic sampling plans being advocated by the U.S. EPA. This near-real-time capability greatly improves the field sampling team's ability to identify which explosives analytes are present at a site and characterize their distribution and concentrations. These capabilities and the low cost of the instrument and sample preparation equipment make this method of explosives residue analysis a good addition to those already endorsed by the US EPA.

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APPENDIX A: ETV PROGRAM GC-TID AND REFERENCE LABORATORY RESULTS FOR 2,4-DNT, RDX, AND TNT (mg/kg)

<i>Order</i>	<i>Soil</i>	<i>Sample</i>	<i>Rep</i>	<i>GC-TID 2,4-DNT</i>	<i>Ref 2,4-DNT</i>	<i>GC-TID RDX</i>	<i>Ref RDX</i>	<i>GC-TID TNT</i>	<i>Ref TNT</i>
1079	Blank	1	1	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
1076	Blank	1	2	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
1062	Blank	1	3	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
1078	Blank	1	4	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
	average								
	% RSD								
1070	Blank	2	1	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
1108	Blank	2	2	<0.5	<51.0	<0.5	<51.0	<0.5	70900.0
1038	Blank	2	3	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
1054	Blank	2	4	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
	average								
	% RSD								
1043	Blank	3	1	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
1052	Blank	3	2	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
1008	Blank	3	3	<0.5	<0.5	<0.5	<0.5	1.1	<0.5
1102	Blank	3	4	<0.5	<0.5	<0.5	<0.5	0.5	<0.5
	average								
	% RSD								
1024	Blank	4	1	<0.5	<0.5	<0.5	<0.5	<0.5	0.9
1018	Blank	4	2	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
1101	Blank	4	3	<0.5	<0.5	<0.5	<0.5	0.7	<0.5
1022	Blank	4	4	<0.5	<0.5	<0.5	<0.5	0.5	<0.5
	average								
	% RSD								
1088	Blank	5	1	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
1046	Blank	5	2	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
1006	Blank	5	3	<0.5	<0.5	<0.5	<0.5	6.3	<0.5
1053	Blank	5	4	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
	average								
	% RSD								
1050	Fort Ord	1	1	<0.5	<0.5	<0.5	0.6	<0.5	<0.5
1073	Fort Ord	1	2	<0.5	<0.5	<0.5	<0.5	<0.5	0.8
1092	Fort Ord	1	3	<0.5	<0.5	<0.5	<0.5	<0.5	0.8
1013	Fort Ord	1	4	<0.5	<0.5	<0.5	0.5	<0.5	<0.5
	average								
	% RSD								
1034	Fort Ord	2	1	<0.5	<0.5	<0.5	<0.5	0.6	0.8
1031	Fort Ord	2	2	<0.5	<0.5	<0.5	<0.5	<0.5	2.1
1098	Fort Ord	2	3	<0.5	<0.5	<0.5	<0.5	3.0	0.8
1067	Fort Ord	2	4	<0.5	<0.5	<0.5	<0.5	0.5	0.8
	average							0.9	1.1
	% RSD							165.1	57.8
1026	Fort Ord	3	1	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
1084	Fort Ord	3	2	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
1066	Fort Ord	3	3	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
1030	Fort Ord	3	4	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
	average								
	% RSD								

Order	Soil	Sample	Rep	GC-TID 2,4-DNT	Ref 2,4-DNT	GC-TID RDX	Ref RDX	GC-TID TNT	Ref TNT
1077	Iowa	1	1	11.0	<51.0	<50.0	<51.0	21000.0	20400.0
1003	Iowa	1	2	<500.0	<0.5	<500.0	<0.5	31000.0	0.8
1021	Iowa	1	3	18.0	<532.0	<50.0	<532.0	23000.0	33400.0
1023	Iowa	1	4	10.0	<50.5	<50.0	<50.5	22000.0	28300.0
	average							24250.0	20525.2
	% RSD							18.9	71.6
1107	Louisiana	1	1	<0.5	<0.5	2500.0	3460.0	150.0	109.0
1090	Louisiana	1	2	<50.0	<0.5	2400.0	3520.0	120.0	120.0
1100	Louisiana	1	3	<50.0	<0.5	2300.0	2140.0	120.0	111.0
1025	Louisiana	1	4	<5.0	<25.0	2200.0	1900.0	99.0	125.0
	average					2350.0	2755.0	122.3	116.3
	% RSD					5.5	31.0	17.2	6.5
1010	Louisiana	2	1	<5.0	<0.5	1400.0	1180.0	66.0	50.0
1027	Louisiana	2	2	<5.0	<0.5	1100.0	1450.0	76.0	51.0
1029	Louisiana	2	3	<5.0	<0.5	1300.0	1170.0	61.0	51.0
1012	Louisiana	2	4	<5.0	<0.5	1200.0	320.0	63.0	10.6
	average					1250.0	1030.0	66.5	40.7
	% RSD					10.3	47.6	10.0	49.3
1082	Louisiana	3	1	<50.0	<0.5	4800.0	4300.0	81.0	205.0
1041	Louisiana	3	2	<50.0	<50.0	3500.0	3550.0	89.0	170.0
1055	Louisiana	3	3	5.5	<50.0	3400.0	4650.0	45.0	300.0
1037	Louisiana	3	4	<5.0	<0.5	4000.0	5850.0	150.0	400.0
	average					3925.0	4587.5	91.3	268.8
	% RSD					16.3	20.9	47.8	38.4
1081	Louisiana	4	1	14.0	80.0	6.1	12.0	80.0	89.0
1007	Louisiana	4	2	8.8	11.4	7.1	10.7	84.0	78.0
1056	Louisiana	4	3	8.5	11.9	6.9	10.8	82.0	81.5
1087	Louisiana	4	4	7.2	9.5	4.6	7.7	73.0	67.5
	average			9.6	28.2	6.2	10.3	79.8	79.0
	% RSD			31.2	122.5	18.4	17.8	6.0	11.3
1097	Milan	1	1	<0.5	<0.5	110.0	149.0	3.3	2.7
1019	Milan	1	2	<0.5	<0.5	130.0	118.0	9.3	1.1
1083	Milan	1	3	<0.5	<0.5	110.0	72.2	0.9	1.4
1039	Milan	1	4	<0.5	<0.5	150.0	308.0	1.1	1.7
	average					125.0	161.8	3.7	1.7
	% RSD					15.3	63.3	107.4	40.3
1014	Milan	2	1	<0.5	<0.5	22.0	34.8	<0.5	<0.5
1074	Milan	2	2	<0.5	<0.5	20.0	16.4	<0.5	<0.5
1064	Milan	2	3	<0.5	<0.5	26.0	28.0	<0.5	<0.5
1072	Milan	2	4	<0.5	<0.5	18.0	22.9	<0.5	<0.5
	average					21.5	25.5	<0.5	<0.5
	% RSD					15.9	30.5	0.0	0.0
1069	Milan	3	1	<50.0	<0.5	7900.0	2350.0	260.0	190.0
1065	Milan	3	2	<50.0	<50.0	3400.0	1950.0	82.0	270.0
1016	Milan	3	3	<50.0	<200.0	4100.0	4080.0	300.0	320.0
1033	Milan	3	4	<50.0	<0.5	3800.0	3880.0	110.0	273.0
	average					4800.0	3065.0	188.0	263.3
	% RSD					43.5	35.0	57.5	20.5
1086	Milan	4	1	<5.0	<50.0	2500.0	2740.0	110.0	220.0
1028	Milan	4	2	<50.0	<0.5	2500.0	2640.0	68.0	260.0
1036	Milan	4	3	<50.0	<0.5	2100.0	2600.0	45.0	80.0
1005	Milan	4	4	<50.0	<0.5	2700.0	3070.0	80.0	162.0
	average					2450.0	2762.5	75.8	180.5
	% RSD					10.3	7.7	35.7	43.3

Order	Soil	Sample	Rep	GC-TID 2,4-DNT	Ref 2,4-DNT	GC-TID RDX	Ref RDX	GC-TID TNT	Ref TNT
1048	Milan	5	1	0.7	2.1	<0.5	<0.5	7.7	11.5
1047	Milan	5	2	0.6	2.7	<0.5	<0.5	7.3	10.2
1060	Milan	5	3	0.7	1.7	<0.5	<0.5	7.1	11.3
1059	Milan	5	4	0.6	1.6	<0.5	<0.5	6.8	10.6
	average			0.7	2.0	<0.5	<0.5	7.2	10.9
	% RSD			8.9	24.7	0.0	0.0	5.2	5.6
1103	Spike/PE	1	1	<0.5	<0.5	<0.5	<0.5	87.0	81.8
1044	Spike/PE	1	2	<0.5	<0.5	<0.5	<0.5	87.0	104.0
1095	Spike/PE	1	3	<0.5	<0.5	<0.5	<0.5	92.0	90.0
1094	Spike/PE	1	4	<0.5	<0.5	<0.5	<0.5	92.0	124.0
	average							89.5	100.0
	% RSD							3.2	18.5
1105	Spike/PE	2	1	<0.5	<0.5	84.0	111.0	<0.5	<0.5
1057	Spike/PE	2	2	<0.5	<0.5	76.0	90.5	<0.5	<0.5
1020	Spike/PE	2	3	<0.5	<0.5	88.0	98.0	2.4	<0.5
1063	Spike/PE	2	4	<0.5	<0.5	74.0	127.0	<0.5	<0.5
	average					80.5	106.6		
	% RSD					8.2	15.0		
1049	Spike/PE	3	1	<0.5	<0.5	49.0	49.5	11.0	8.4
1001	Spike/PE	3	2	<0.5	<0.5	56.0	45.0	10.0	7.6
1058	Spike/PE	3	3	<0.5	<0.5	47.0	63.5	9.9	10.0
1061	Spike/PE	3	4	<0.5	<0.5	46.0	51.0	10.0	8.5
	average					49.5	52.3	10.2	8.6
	% RSD					9.1	15.2	5.1	11.6
1104	Spike/PE	4	1	<0.5	<0.5	7.6	9.1	45.0	47.5
1096	Spike/PE	4	2	<0.5	<0.5	9.7	8.4	50.0	48.5
1071	Spike/PE	4	3	<0.5	<0.5	8.9	8.6	45.0	48.5
1106	Spike/PE	4	4	<0.5	<0.5	8.7	9.1	48.0	47.0
	average					8.7	8.8	47.0	47.9
	% RSD					9.9	4.0	5.2	1.6
1068	Spike/PE	5	1	<0.5	<0.5	440.0	460.0	260.0	230.0
1004	Spike/PE	5	2	<5.0	<0.5	490.0	455.0	240.0	205.0
1075	Spike/PE	5	3	<5.0	<0.5	490.0	705.0	260.0	435.0
1045	Spike/PE	5	4	<0.5	<0.5	450.0	445.0	260.0	205.0
	average					467.5	516.3	255.0	268.8
	% RSD					5.6	24.4	3.9	41.5
1099	Spike/PE	6	1	<5.0	<0.5	210.0	260.0	480.0	535.0
1042	Spike/PE	6	2	<5.0	<25.0	220.0	255.0	480.0	505.0
1093	Spike/PE	6	3	<5.0	<0.5	230.0	335.0	480.0	675.0
1017	Spike/PE	6	4	<0.5	<0.5	270.0	250.0	500.0	510.0
	average					232.5	275.0	485.0	556.3
	% RSD					11.3	14.6	2.1	14.4
1002	Volunteer	1	1	<500.0	<50.0	<500.0	<50.0	190000.0	108000.0
1091	Volunteer	1	2	59.0	<25.0	<50.0	<25.0	110000.0	75500.0
1089	Volunteer	1	3	60.0	19.0	<50.0	<5.0	110000.0	117000.0
1015	Volunteer	1	4	67.0	<250.0	<50.0	<250.0	94000.0	61000.0
	average							126000.0	90375.0
	% RSD							34.4	29.3
1085	Volunteer	2	1	30.0	<53.2	<50.0	<53.2	9000.0	11300.0
1051	Volunteer	2	2	29.0	<538.0	<50.0	<538.0	6200.0	12600.0
1011	Volunteer	2	3	35.0	<5.4	<50.0	6.5	8300.0	26200.0
1009	Volunteer	2	4	34.0	45.2	<50.0	<5.4	9400.0	8920.0
	average			32.0				8225.0	14755.0
	% RSD			9.2				17.3	52.7

<i>Order</i>	<i>Soil</i>	<i>Sample</i>	<i>Rep</i>	<i>GC-TID</i> <i>2,4-DNT</i>	<i>Ref</i> <i>2,4-DNT</i>	<i>GC-TID</i> <i>RDX</i>	<i>Ref</i> <i>RDX</i>	<i>GC-TID</i> <i>TNT</i>	<i>Ref</i> <i>TNT</i>
1035	Volunteer	3	1	0.7	2.0	<0.5	<0.5	9.9	12.0
1032	Volunteer	3	2	0.7	3.0	<0.5	<0.5	8.0	10.3
1040	Volunteer	3	3	0.6	2.2	<0.5	<0.5	7.7	13.8
1080	Volunteer	3	4	0.6	2.2	<0.5	<0.5	7.7	10.4
	average			0.7	2.4			8.3	11.6
	% RSD			8.9	18.9			12.7	14.2